SHALE HYDRATION INHIBITION AGENT AND METHOD OF USE

BACKGROUND

In rotary drilling of subterranean wells numerous functions and characteristics are expected of a drilling fluid. A drilling fluid should circulate throughout the well and carry cuttings from beneath the bit, transport the cuttings up the annulus, and allow their separation at the surface. At the same time, the drilling fluid is expected to cool and clean the drill bit, reduce friction between the drill string and the sides of the hole, and maintain stability in the borehole's uncased sections. The drilling fluid should also form a thin, low permeability filter cake that seals openings in formations penetrated by the bit and act to reduce the unwanted influx of formation fluids from permeable rocks.

Drilling fluids are typically classified according to their base material. In oil base fluids, solid particles are suspended in oil, and water or brine may be emulsified with the oil. The oil is typically the continuous phase. In water base fluids, solid particles are suspended in water or brine, and oil may be emulsified in the water. The water is typically the continuous phase. Pneumatic fluids are a third class of drilling fluids in which a high velocity stream of air or natural gas removes drill cuttings.

Three types of solids are usually found in water base drilling fluids: 1) clays and organic colloids added to provide necessary viscosity and filtration properties; 2) heavy minerals whose function is to increase the drilling fluid's density; and 3) formation solids that become dispersed in the drilling fluid during the drilling operation.

The formation solids that become dispersed in a drilling fluid are typically the cuttings produced by the drill bit's action and the solids produced by borehole instability. Where the formation solids are clay minerals that swell, the presence of either type of formation solids in the drilling fluid can greatly increase drilling time and costs.

Clay minerals are generally crystalline in nature. The structure of a clay's crystals determines its properties. Typically, clays have a flaky, mica-type structure. Clay flakes are made up of a number of crystal platelets stacked face-to-face. Each platelet is called a unit layer, and the surfaces of the unit layer are called basal surfaces.

A unit layer is composed of multiple sheets. One sheet is called the octahedral sheet, it is composed of either aluminum or magnesium atoms octahedrally coordinated with the oxygen atoms of hydroxyls. Another sheet is called the tetrahedral sheet. The tetrahedral sheet consists of silicon atoms tetrahedrally coordinated with oxygen atoms.

Sheets within a unit layer link together by sharing oxygen atoms. When this linking occurs between one octahedral and one tetrahedral sheet, one basal surface consists of exposed oxygen atoms while the other basal surface has exposed hydroxyls. It is also quite common for two tetrahedral sheets to bond with one octahedral sheet by sharing oxygen atoms. The resulting structure, known as the Hoffman structure, has an octahedral sheet that is sandwiched between the two tetrahedral sheets. As a result, both basal surfaces in a Hoffman structure are composed of exposed oxygen atoms.

The unit layers stack together face-to-face and are held in place by weak attractive forces. The distance between corresponding planes in adjacent unit layers is called the c-spacing. A clay crystal structure with a unit layer consisting of three sheets typically has a c-spacing of about 9.5×10^{-7} mm.

In clay mineral crystals, atoms having different valences commonly will be positioned within the sheets of the structure to create a negative potential at the crystal surface. In that case, a cation is adsorbed on the surface. These adsorbed cations are called exchangeable cations because they may chemically trade places with other cations when the clay crystal is suspended in water. In addition, ions may also be adsorbed on the clay crystal edges and exchange with other ions in the water.

The type of substitutions occurring within the clay crystal structure and the exchangeable cations adsorbed on the crystal surface greatly affect clay swelling, a property of primary importance in the drilling fluid industry. Clay swelling is a phenomenon in which water molecules surround a clay crystal structure and position themselves to increase the structure's c-spacing thus resulting in an increase in volume. Two types of swelling may occur.

Surface hydration is one type of swelling in which water molecules are adsorbed on crystal surfaces. Hydrogen bonding holds a layer of water molecules to the oxygen atoms exposed on the crystal surfaces. Subsequent layers of water molecules align to

form a quasi-crystalline structure between unit layers, which results in an increased c-spacing. Virtually all types of clays swell in this manner.

Osmotic swelling is a second type of swelling. Where the concentration of cations between unit layers in a clay mineral is higher than the cation concentration in the surrounding water, water is osmotically drawn between the unit layers and the c-spacing is increased. Osmotic swelling results in larger overall volume increases than surface hydration. However, only certain clays, like sodium montmorillonite, swell in this manner.

Exchangeable cations found in clay minerals are reported to have a significant impact on the amount of swelling that takes place. The exchangeable cations compete with water molecules for the available reactive sites in the clay structure. Generally cations with high valences are more strongly adsorbed than ones with low valences. Thus, clays with low valence exchangeable cations will swell more than clays whose exchangeable cations have high valences.

In the North Sea and the United States Gulf Coast, drillers commonly encounter argillaceous sediments in which the predominant clay mineral is sodium montmorillonite (commonly called "gumbo shale"). Sodium cations are predominately the exchangeable cations in gumbo shale. As the sodium cation has a low positive valence (i.e. formally a +1 valence), it easily disperses into water. Consequently, gumbo shale is notorious for its swelling.

Clay swelling during the drilling of a subterranean well can have a tremendous adverse impact on drilling operations. The overall increase in bulk volume accompanying clay swelling impedes removal of cuttings from beneath the drill bit, increases friction between the drill string and the sides of the borehole, and inhibits formation of the thin filter cake that seals formations. Clay swelling can also create other drilling problems such as loss of circulation or stuck pipe that slow drilling and increase drilling costs. Thus, given the frequency in which gumbo shale is encountered in drilling subterranean wells, the development of a substance and method for reducing clay swelling remains a continuing challenge in the oil and gas exploration industry.

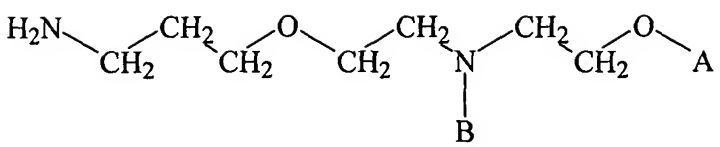
One method to reduce clay swelling is to use salts in drilling fluids. Salts generally reduce the swelling of clays. However, salts flocculate the clays resulting in both high fluid losses and an almost complete loss of thixotropy. Further, increasing salinity often decreases the functional characteristics of drilling fluid additives.

Another method for controlling clay swelling is to use organic shale inhibitor molecules in drilling fluids. It is believed that the organic shale inhibitor molecules are adsorbed on the surfaces of clays with the added organic shale inhibitor competing with water molecules for clay reactive sites and thus serve to reduce clay swelling.

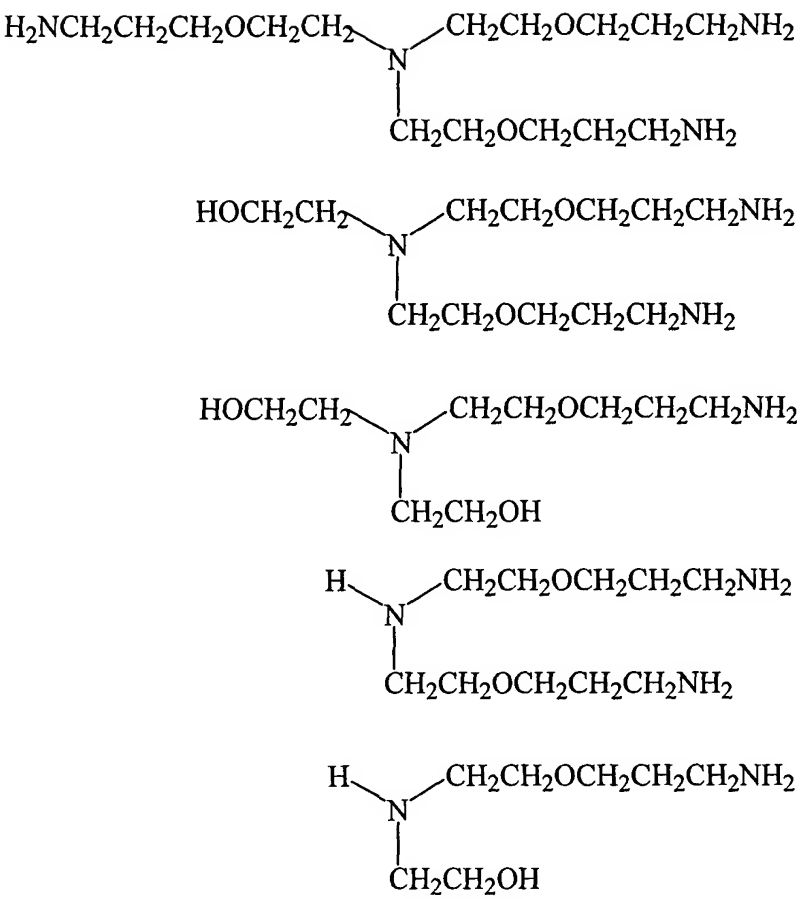
It is important that the driller of subterranean wells be able to control the rheological properties of drilling fluids by using additives, including organic shale inhibitor molecules. In the oil and gas industry today it is desirable that additives work both onshore and offshore and in fresh and salt water environments. In addition, as drilling operations impact on plant and animal life, drilling fluid additives should have low toxicity levels and should be easy to handle and to use to minimize the dangers of environmental pollution and harm to operators. Any drilling fluid additive should also provide desirable results but should not inhibit the desired performance of other additives. The development of such additives will help the oil and gas industry to satisfy the long felt need for superior drilling fluid additives which act to control the swelling of the clay and drilled formations without adversely effecting the rheological properties of drilling fluids. The claimed subject matter addresses this need.

SUMMARY

Upon consideration of the present disclosure, one of skill in the art should understand and appreciate that one illustrative embodiment of the claimed subject matter includes a water-base drilling fluid for use in drilling wells through a formation containing a shale which swells in the presence of water. In such an illustrative embodiment, the drilling fluid includes, an aqueous based continuous phase, a weighting agent, and a shale hydration inhibition agent. The shale hydration inhibition agent should have the general formula:



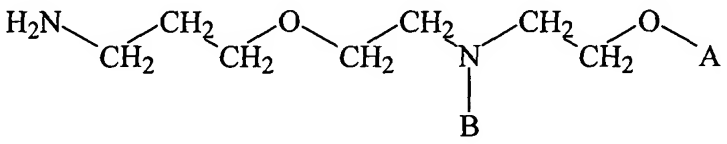
in which A is independently selected from H and $CH_2CH_2CH_2NH_2$; and in which B is independently selected from H, CH_2CH_2OH, $CH_2CH_2OCH_2CH_2CH_2NH_2$ and $CH_2CH_2CH_2NH_2$. The shale hydration inhibition agent is present in sufficient concentration to substantially reduce the swelling of shale drilling cuttings upon contact with the drilling fluid. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of a hydrogenation reaction of the product of the reaction of triethanolamine and acrylonitrile. Alternatively the shale hydration inhibition agent may be the reaction product of a hydrogenation reaction of the product of the reaction of diethanolamine and acrylonitrile. In a particularly preferred illustrative embodiment, the shale hydration inhibition agent is selected from:



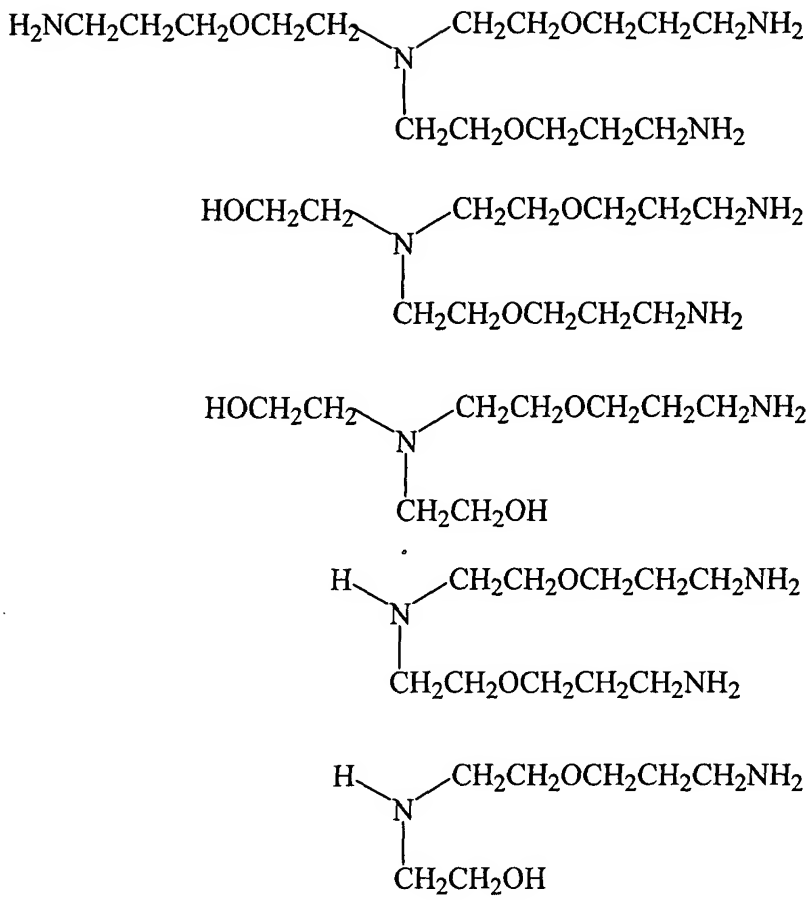
as well as mixtures of these. The illustrative drilling fluid is formulated such that the aqueous based continuous phase is selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected from mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyarcylamides, and the like. A weighting material such as barite, calcite, hematite, iron oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative fluid. The illustrative fluid may also include a wide variety of conventional components of aqueous based

drilling fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

The scope of the claimed subject matter also encompasses a fracturing fluid for use in a subterranean well in which the subterranean well penetrates through one or more subterranean formation composed of a shale that swells in the presence of water. One illustrative fluid is formulated to include an aqueous based continuous phase, a viscosifying agent and a shale hydration inhibition agent which is present in sufficient concentration to substantially reduce the swelling of shale. In one illustrative embodiment, the shale hydration inhibition agent has the formula:



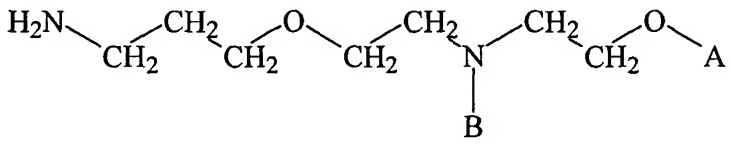
in which A is independently selected from H and $CH_2CH_2CH_2NH_2$; and in which B is independently selected from H, CH_2CH_2OH, $CH_2CH_2OCH_2CH_2CH_2NH_2$ and $CH_2CH_2CH_2NH_2$. Alternatively, the shale hydration inhibition agent of the illustrative fluid may be selected from



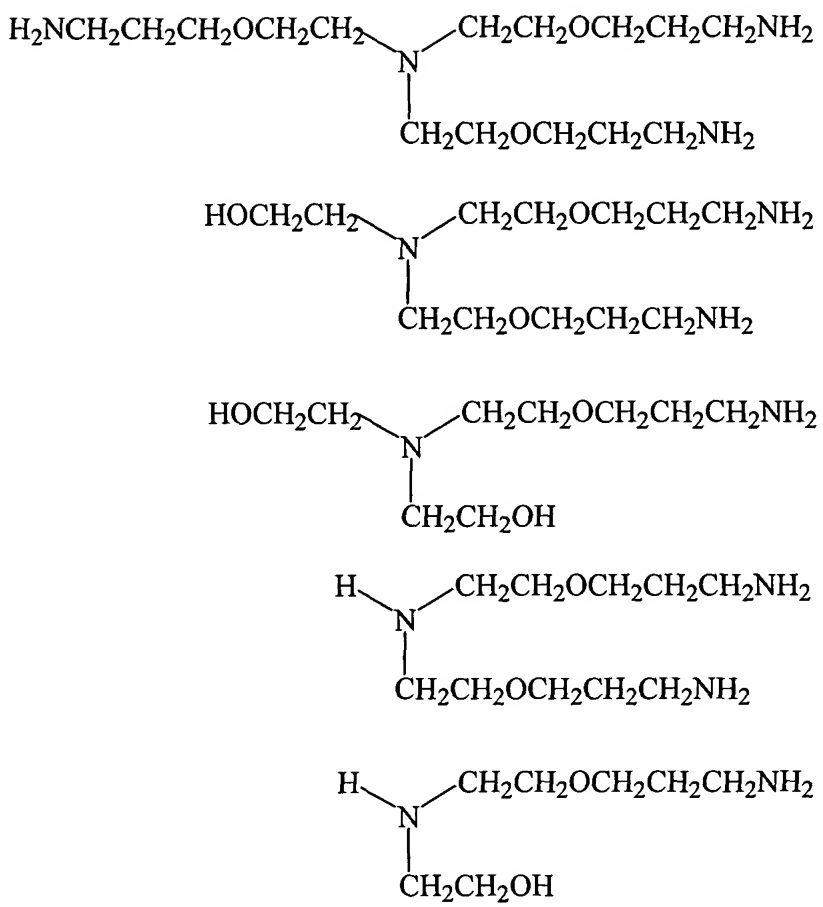
as well as mixtures of these. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of a hydrogenation reaction of the product of the reaction of triethanolamine and acrylonitrile. Alternatively the shale hydration inhibition agent may be the reaction product of a hydrogenation reaction of the product of the reaction of diethanolamine and acrylonitrile. The illustrative fluid is formulated such that the aqueous based continuous phase may be selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyarcylamides, and the like. A weighting material such as barite, calcite, hematite, iron

oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative fluid. The illustrative fluid may also include a wide variety of conventional components of fracturing fluids, such as propants such as sand, gravel, glass beads, ceramic materials and the like, acid release agents, fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

It should also be appreciated that the claimed subject matter inherently includes components such as: an aqueous based continuous phase; a swellable shale material; and a shale hydration inhibition agent present in sufficient concentration to substantially reduce the swelling of the swellable shale material. Such a composition may be formed during the course of drilling a subterranean well, but also may be deliberately made if drill cuttings reinjection is to be carried out. In one illustrative embodiment, the shale hydration inhibition agent has the formula:



in which A is independently selected from H and $CH_2CH_2CH_2NH_2$; and in which B is independently selected from H, CH_2CH_2OH, $CH_2CH_2OCH_2CH_2CH_2NH_2$ and $CH_2CH_2CH_2NH_2$. Alternatively, the shale hydration inhibition agent of the illustrative composition may be selected from



as well as mixtures of these. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of a hydrogenation reaction of the product of the reaction of triethanolamine and acrylonitrile. Alternatively the shale hydration inhibition agent may be the reaction product of a hydrogenation reaction of the product of the reaction of diethanolamine and acrylonitrile. The illustrative composition is formulated such that the aqueous based continuous phase may be selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyarcylamides, and the like. A weighting material such as barite, calcite, hematite, iron

oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative composition. The illustrative composition may also include a wide variety of conventional components of drilling and well bore fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

One of skill in the art should appreciate that the fluids of the claimed subject matter are useful during the course of the drilling, cementing, fracturing, maintenance and production, workover, abandonment a well as other operations associated with subterranean wells. The claimed subject matter also includes a method of disposing of drill cuttings into a subterranean formation. It should also be appreciated by one of skill in the art that the claimed subject matter inherently includes a method of reducing the swelling of shale clay in a well, the method including circulating in the well a water-base drilling fluid formulated as is substantially disclosed herein. These and other features of the claimed subject matter are more fully set forth in the following description of illustrative embodiments of the claimed subject matter.

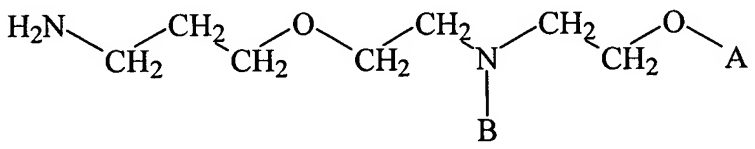
DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

The claimed subject matter is directed to a water-base drilling fluid for use in drilling wells through a formation containing a shale which swells in the presence of water. Generally the drilling fluid of the claimed subject matter may be formulated to include an aqueous continuous phase and a shale hydration inhibition agent. As disclosed below, the drilling fluids of the claimed subject matter may optionally include additional components, such as weighting agents, viscosity agents, fluid loss control agents, bridging agents, lubricants, anti-bit balling agents, corrosion inhibition agents, alkali reserve materials and buffering agents, surfactants and suspending agents, rate of penetration enhancing agents and the like that one of skill in the art should understand may be added to an aqueous based drilling fluid.

The aqueous based continuous phase may generally be any water based fluid phase that is compatible with the formulation of a drilling fluid and is compatible with the shale hydration inhibition agents disclosed herein. In one preferred embodiment, the aqueous based continuous phase is selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds and mixtures thereof. The amount of the aqueous based continuous phase should be sufficient to form a water based drilling fluid. This amount may range from nearly 100% of the drilling fluid to less than 30 % of the drilling fluid by volume. Preferably, the aqueous based continuous phase is from about 95 to about 30 % by volume and preferably from about 90 to about 40 % by volume of the drilling fluid.

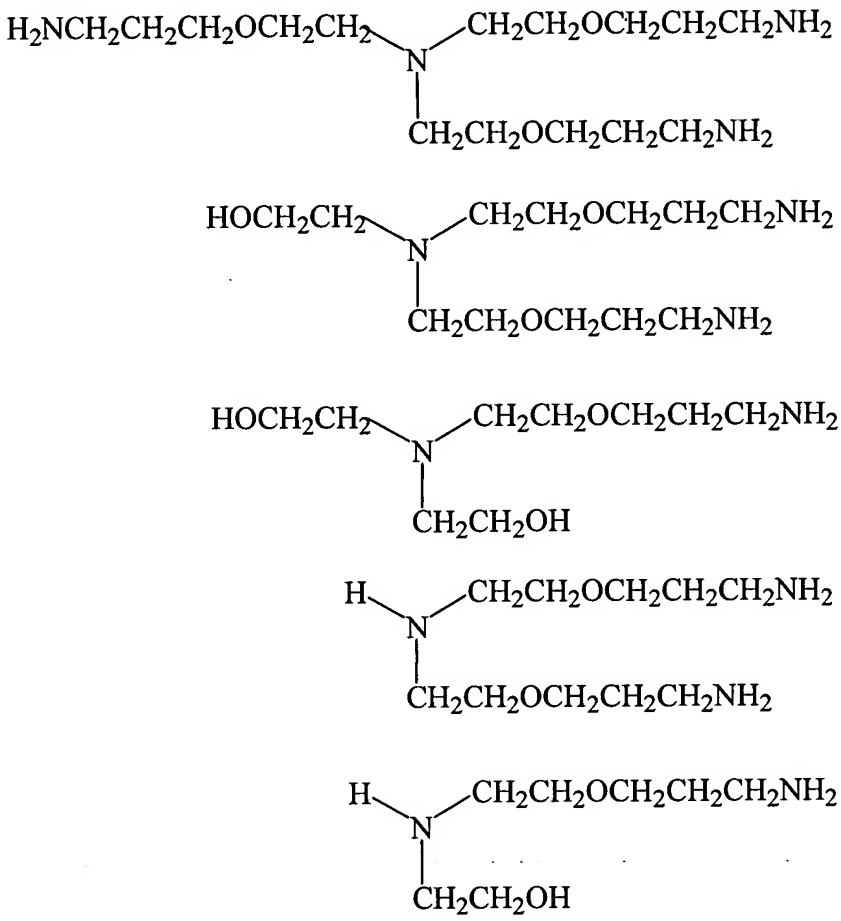
A shale hydration inhibition agent is included in the formulation of the drilling fluids of the claimed subject matter so that the hydration of shale and shale like formations is inhibited. Thus, the shale hydration inhibition agent should be present in sufficient concentration to reduce either or both the surface hydration based swelling and/or the osmotic based swelling of the shale clay. The exact amount of the shale hydration inhibition agent present in a particular drilling fluid formulation can be determined by a trial and error method of testing the combination of drilling fluid and shale clay formation encountered. Generally however, the shale hydration inhibition agent of the claimed subject matter may be used in drilling fluids in a concentration from about 1 to about 18 pounds per barrel (lbs/bbl or ppb) and more preferably in a concentration from about 2 to about 12 pounds per barrel of drilling fluid.

The shale hydration inhibition agent of the claimed subject matter should have the general formula:



in which A is independently selected from H and $CH_2CH_2CH_2NH_2$; and in which B is independently selected from H, CH_2CH_2OH, $CH_2CH_2OCH_2CH_2CH_2NH_2$ and $CH_2CH_2CH_2NH_2$. The shale hydration inhibition agent is present in sufficient

concentration to substantially reduce the swelling of shale drilling cuttings upon contact with the drilling fluid. In a particularly preferred illustrative embodiment, the shale hydration inhibition agent is selected from:



as well as mixtures of these.

When considering the illustrative shale hydration inhibition agents disclosed above, one skilled in organic synthesis should recognize that a wide variety of synthetic reaction pathways can be used to reach the above target molecules. It has been found that one desirable and economic way to achieve the target compounds is the reaction of triethanolamine and acrylonitrile followed by hydrogenation of the resulting reaction product. Alternatively the shale hydration inhibition agent may be the reaction product of a hydrogenation reaction of a product of the reaction of diethanolamine and acrylonitrile. The techniques, required apparatus, and reaction conditions for carrying out such

reactions should be easily obtained from the appropriate literature by one of skill in the art of organic synthesis. In some instances the above compounds may be commercially available from specialty chemical suppliers although their use and application may be in a field other than drilling fluid formulation.

The drilling fluids of the claimed subject matter can include a weight material in order to increase the density of the fluid. The primary purpose for such weighting materials is to increase the density of the drilling fluid so as to prevent kick-backs and blow-outs. One of skill in the art should know and understand that the prevention of kick-backs and blow-outs is important to the safe day to day operations of a drilling rig. Thus the weight material is added to the drilling fluid in a functionally effective amount largely dependent on the nature of the formation being drilled. Weight materials suitable for use in the formulation of the drilling fluids of the claimed subject matter may be generally selected from any type of weighting materials be it in solid, particulate form, suspended in solution, dissolved in the aqueous phase as part of the preparation process or added afterward during drilling. It is preferred that the weight material be selected from the group including barite, hematite, iron oxide, calcium carbonate, magnesium carbonate, organic and inorganic salts, and mixtures and combinations of these compounds and similar such weight materials that may be utilized in the formulation of drilling fluids.

The drilling fluids of the claimed subject matter can include a viscosifying agent in order to alter or maintain the rheological properties of the fluid. The primary purpose for such viscosifying agents is to control the viscosity and potential changes in viscosity of the drilling fluid. Viscosity control is particularly important because often a subterranean formation may have a temperature significantly higher than the surface temperature. Thus a drilling fluid may undergo temperature extremes of nearly freezing temperatures to nearly the boiling temperature of water or higher during the course of its transit from the surface to the drill bit and back. One of skill in the art should know and understand that such changes in temperature can result in significant changes in the rheological properties of fluids. Thus in order to control and/or moderate the rheology changes, viscosity agents and rheology control agents may be included in the formulation

of the drilling fluid. Viscosifying agents suitable for use in the formulation of the drilling fluids of the claimed subject matter may be generally selected from any type of viscosifying agents suitable for use in aqueous based drilling fluids. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyarcylamides, and the like.

In addition to the components noted above, the claimed drilling fluids may also be formulated to include materials generically referred to as alkali reserve and alkali buffering agent, gelling materials, thinners, and fluid loss control agents, as well as other compounds and materials which are optionally added to water base drilling fluid formulations. Of these additional materials, each can be added to the formulation in a concentration as rheologically and functionally required by drilling conditions.

One of skill in the art should appreciate that lime is the principle alkali reserve agent utilized in formulating water based drilling fluids. Alkali buffering agents, such as cyclic organic amines, sterically hindered amines, amides of fatty acids and the like may also be included to serve as a buffer against the loss of the alkali reserve agent. The drilling fluid may also contain anticorrosion agents as well to prevent corrosion of the metal components of the drilling operational equipment. Gelling materials are also often used in aqueous based drilling fluids and these include bentonite, sepiolite, clay, attapulgite clay, anionic high-molecular weight polymers and biopolymers. Thinners such as lignosulfonates are also often added to water-base drilling fluids. Typically lignosulfonates, modified lignosulfonates, polyphosphates and tannins are added. In other embodiments, low molecular weight polyacrylates can also be added as thinners. Thinners are added to a drilling fluid to reduce flow resistance and control gelation tendencies. Other functions performed by thinners include reducing filtration and filter cake thickness, counteracting the effects of salts, minimizing the effects of water on the formations drilled, emulsifying oil in water, and stabilizing mud properties at elevated temperatures.

A variety of fluid loss control agents may be added to the drilling fluids of the claimed subject matter that are generally selected from a group consisting of synthetic

organic polymers, biopolymers, and mixtures thereof. The fluid loss control agents such as modified lignite, polymers, modified starches and modified celluloses may also be added to the water base drilling fluid system of this invention. In one embodiment it is preferred that the additives of the invention should be selected to have low toxicity and to be compatible with common anionic drilling fluid additives such as polyanionic carboxymethylcellulose (PAC or CMC), polyacrylates, partially-hydrolyzed polyacrylamides (PHPA), lignosulfonates, xanthan gum, mixtures of these and the like.

The drilling fluid of the claimed subject matter may further contain an encapsulating agent generally selected from the group consisting of synthetic organic, inorganic and bio-polymers and mixtures thereof. The role of the encapsulating agent is to absorb at multiple points along the chain onto the clay particles, thus binding the particles together and encapsulating the cuttings. These encapsulating agents help improve the removal of cuttings with less dispersion of the cuttings into the drilling fluids. The encapsulating agents may be anionic, cationic, amphoteric, or non-ionic in nature.

Other additives that could be present in the drilling fluids of the claimed subject matter include products such as lubricants, penetration rate enhancers, defoamers, fluid loss circulation products and so forth. Such compounds should be known to one of ordinary skill in the art of formulating aqueous based drilling fluids.

The following examples are included to demonstrate preferred embodiments of the claimed subject matter. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the claimed subject matter, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the scope of the claimed subject matter.

Unless otherwise stated, all starting materials are commercially available and standard laboratory techniques and equipment are utilized. The tests were conducted in

accordance with the procedures in API Bulletin RP 13B-2, 1990. The following abbreviations are sometimes used in describing the results discussed in the examples:

"PV" is plastic viscosity (CPS) which is one variable used in the calculation of viscosity characteristics of a drilling fluid.

"YP" is yield point (lbs/100 ft^2)which is another variable used in the calculation of viscosity characteristics of drilling fluids.

"GELS" (lbs/100 ft^2)is a measure of the suspending characteristics and the thixotropic properties of a drilling fluid.

"F/L" is API fluid loss and is a measure of fluid loss in milliliters of drilling fluid at 100 psi.

Example 1

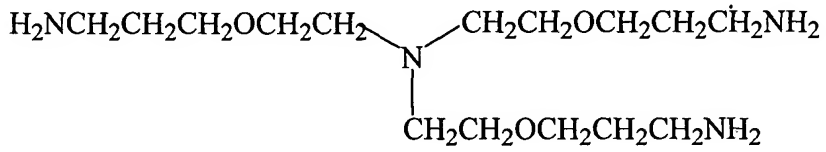
The following drilling muds are formulated to illustrate the claimed subject matter:

	A	B	C
Fresh Water	259.45 ppb	259.45 ppb	259.45 ppb
Sea Salt	11.09 ppb	11.09 ppb	11.09 ppb
Technical grade sodium chloride (Driller's salt)	66.01 ppb	66.01 ppb	66.01 ppb
UltraCap	2.0 ppb	2.0 ppb	2.0 ppb
UltraFree	10.5 ppb	10.5 ppb	10.5 ppb
PolyPac	2.0 ppb	2.0 ppb	2.0 ppb
DuoVis	0.75 ppb	0.75 ppb	0.75 ppb
Rev Dust	25.0 ppb	25.0 ppb	25.0 ppb
Barite	123.18 ppb	123.18 ppb	123.18 ppb
RMR 13-21A	10.5 ppb		
RMR 13-21B		10.5 ppb	
RMR 13-35			10.5 ppb

In the above mud formulation the following commercially available compounds have been used in the formulation of the drilling fluid, but one of skill in the art should appreciate that other similar compounds may be used instead.

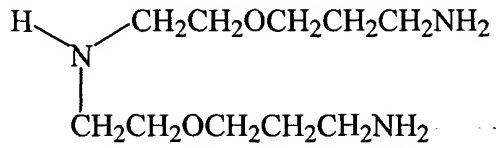
UltraCap	Cationic polyacrylamide availale from M-I LLC.
UltraFree	Mixutre of surfactants and lubricants available from M-I LLC
PolyPac	Poly anionic cellulose
DuoVis	Natural polymeric viscosifier, such as xanthan gum, starches.

In the above mud formulation the following shale inhibitors are utilized: RMR 13-21A is a triethanolaminetriamine having the formula



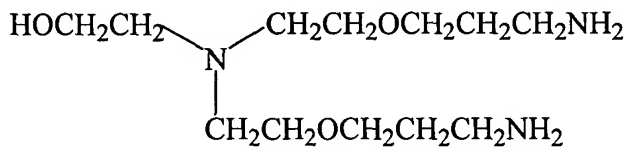
and which is commercially available form Champion Chemicals.

RMR 13-21B is a diethanolaminediamine having the formula



and which is commercially available from Champion Chemicals

RMR 13-35 is a triethanolamine diamine having the formula



and which is commercially available from Champion Chemical.

The properties of the above muds as well as a base mud (i.e. a mud in which there is no shale inhibitor) are measured and give the following exemplary data:

Properties	Base Mud	A	B	C
Viscosity (cps) at 600 rpm	81	101	98	101
300 rpm	51	62	59	65
200 rpm	39	48	46	50
100 rpm	26	33	30	33
6 rpm	7	9	8	10
3 rpm	5	9	6	8
Gels 10 sec.	7	11	7	9
10 min.	7	13	9	12
PV	30	39	39	36
YP	21	23	20	29
F/L	7.8	6.4	5.4	5.2

Dispersion tests are run with Arne Clay cuttings by hot rolling 10 g of cuttings in a one-barrel equivalent of mud for 16 hours at 150° F. After hot rolling the remaining cuttings are screened using a 20 mesh screen and washed with 10% potassium chloride water, dried and weighed to obtain the percentage recovered. The results of this evaluation are given in the following Table and shows the improved shale inhibition performance of shale inhibition agents of this invention.

(% cuttings recovered)	Base Mud	A	B
Arne	76.7	88.0	88.6

To further demonstrate the performance of the drilling fluids formulated in accordance with the teachings of this invention, a test using a bulk hardness tester is conducted. A BP Bulk Hardness Tester is a device designed to give an assessment of the hardness of shale cuttings exposed to drilling fluids, which in turn can be related to the inhibiting properties of the drilling fluid being evaluated. In this test, shale cuttings are hot rolled in the test drilling fluid at 150°F for 16 hours. Shale cuttings are screened and

then placed into a BP Bulk Hardness Tester. The equipment is closed and using a torque wrench the force used to extrude the cuttings through a plate with holes in it is recorded. Depending on the hydration state and hardness of the cuttings and the drilling fluid used, a plateau region in torque is reached as extrusion of the cuttings begins to take place. Alternatively, the torque may continue to rise which tends to occur with harder cutting samples. Therefore, the higher the torque number obtained, the more inhibitive the drilling fluid system is considered. Illustrative data obtained using the three different mud formulations with two different cuttings are given below.

Arne Clay	Bulk Hardness: (values in inch/lbs) Mud Formulation			
Turn No.	Base Mud	A	B	C
8	-	15	15	10
9	10	40	40	50
10	15	130	130	80
11	20	170	170	100
12	20	190	180	100
13	20	215	200	100
14	20	250	250	120
15	30	D/S	D/S	210

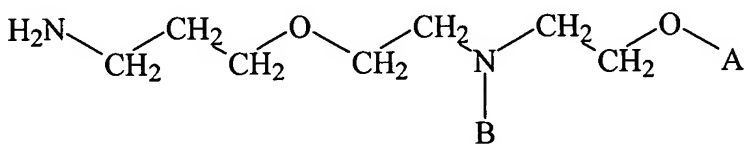
In the above table, D indicates formation of a disk; S indicates the formation of spaghetti like extrudates.

Foss Eikeland Clay	Bulk Hardness: (values in inch/lbs) Mud Formulation			
Turn No.	Base Mud	A	B	C
8	-	10	10	10
9	-	30	25	30
10	15	185	160	200
11	85	320	350	280
12	110	350	D/S	300
13	120	D/S		350
14	160			D/S

In the above table, D indicates contact of the disk; S indicates the formation of spaghetti like extrudates.

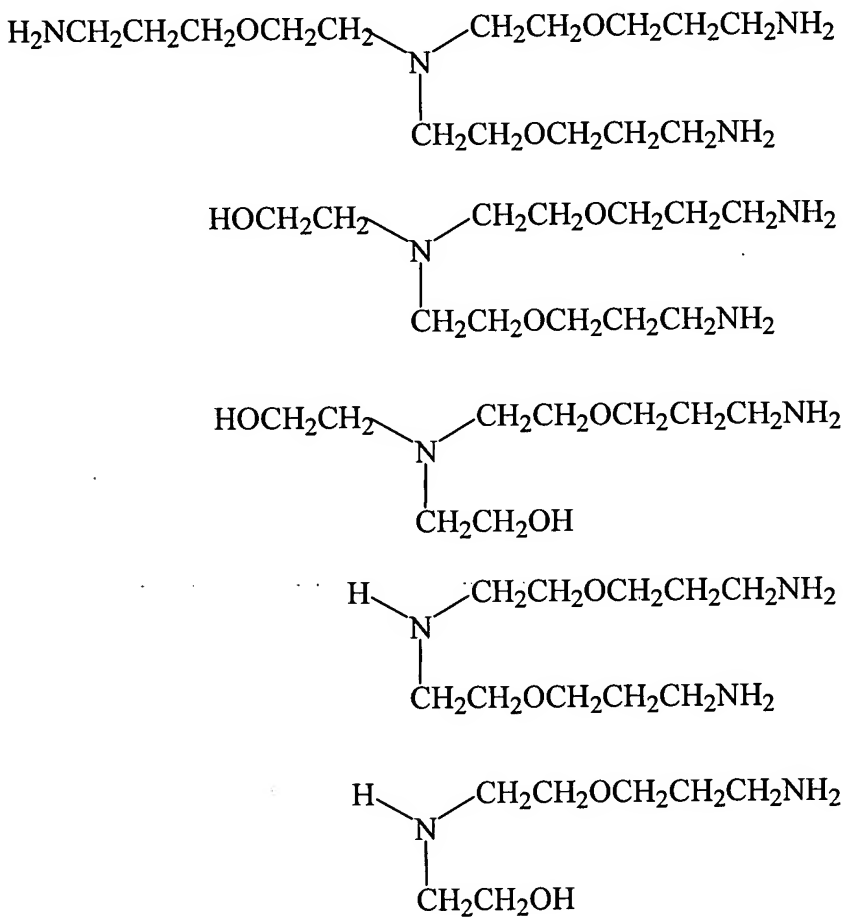
Upon review of the above data, one skilled in the art should observe that drilling fluids formulated according to the teachings of this invention prevent the hydration of various types of shale clays and thus are likely to provide good performance in drilling subterranean wells encountering such shale clays.

In view of the above disclosure, one of skill in the art should understand and appreciate that one illustrative embodiment of the claimed subject matter includes a water-base drilling fluid for use in drilling wells through a formation containing a shale which swells in the presence of water. In such an illustrative embodiment, the drilling fluid includes, an aqueous based continuous phase, a weighting agent, and a shale hydration inhibition agent. The shale hydration inhibition agent should have the general formula:



in which A is independently selected from H and $CH_2CH_2CH_2NH_2$; and in which B is independently selected from H, CH_2CH_2OH, $CH_2CH_2OCH_2CH_2CH_2NH_2$ and

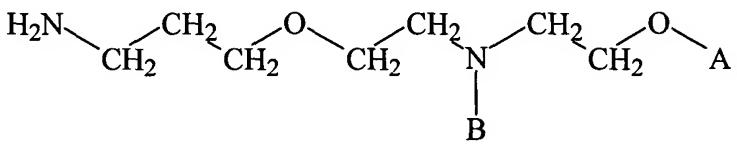
$CH_2CH_2CH_2NH_2$. The shale hydration inhibition agent is present in sufficient concentration to substantially reduce the swelling of shale drilling cuttings upon contact with the drilling fluid. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of a hydrogenation reaction of the product of the reaction of triethanolamine and acrylonitrile. Alternatively the shale hydration inhibition agent may be the reaction product of a hydrogenation reaction of the product of the reaction of diethanolamine and acrylonitrile. In a particularly preferred illustrative embodiment, the shale hydration inhibition agent is selected from:



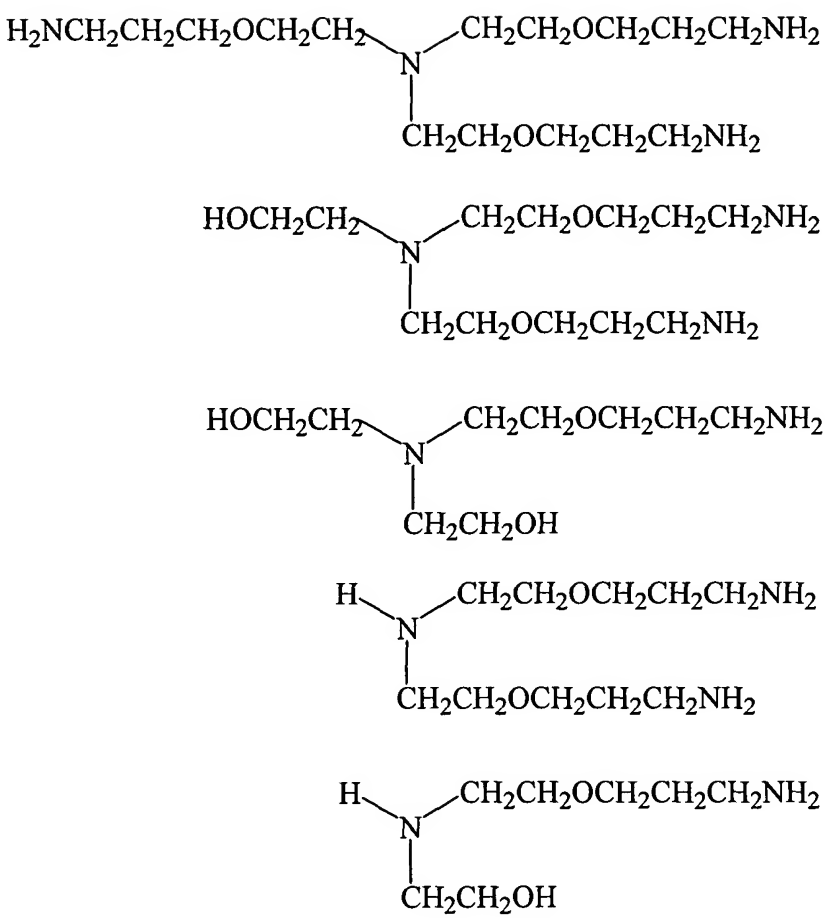
as well as mixtures of these. The illustrative drilling fluid is formulated such that the aqueous based continuous phase is selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of

skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyarcylamides, and the like. A weighting material such as barite, calcite, hematite, iron oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative fluid. The illustrative fluid may also include a wide variety of conventional components of aqueous based drilling fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

The scope of the claimed subject matter also encompasses a fracturing fluid for use in a subterranean well in which the subterranean well penetrates through one or more subterranean formations composed of a shale that swells in the presence of water. One illustrative fluid is formulated to include an aqueous based continuous phase, a viscosifying agent and a shale hydration inhibition agent which is present in sufficient concentration to substantially reduce the swelling of shale. In one illustrative embodiment, the shale hydration inhibition agent has the formula:



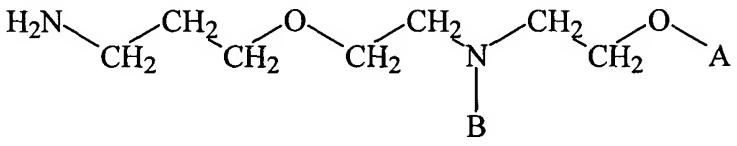
in which A is independently selected from H and $CH_2CH_2CH_2NH_2$; and in which B is independently selected from H, CH_2CH_2OH, $CH_2CH_2OCH_2CH_2CH_2NH_2$ and $CH_2CH_2CH_2NH_2$. Alternatively, the shale hydration inhibition agent of the illustrative fluid may be selected from



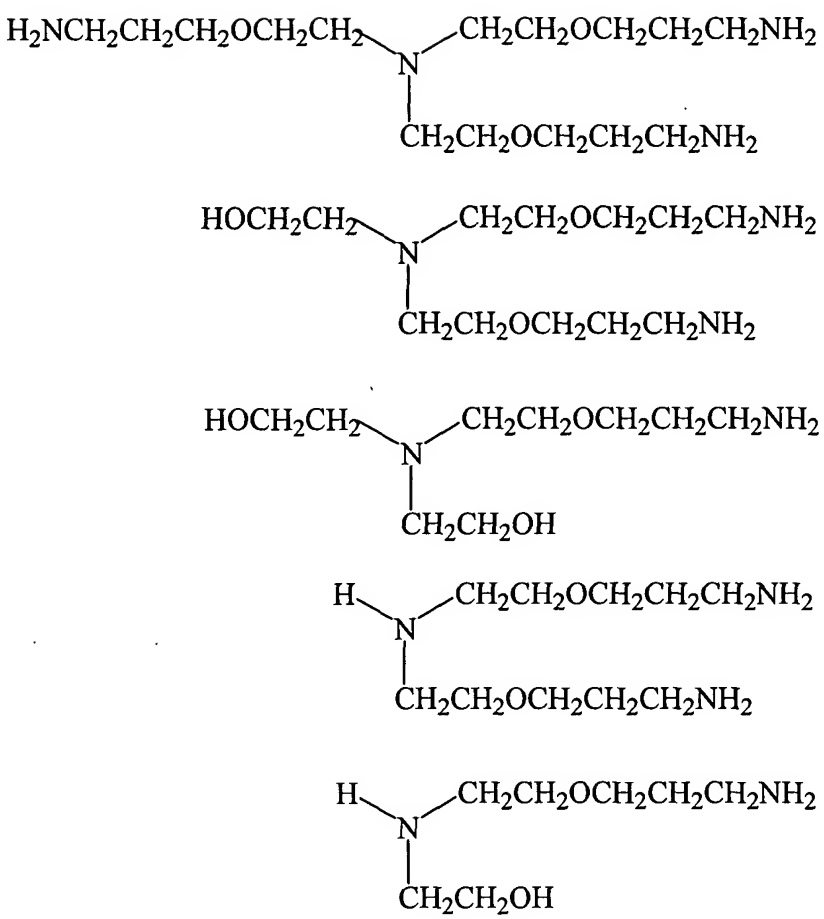
as well as mixtures of these. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of a hydrogenation reaction of the product of the reaction of triethanolamine and acrylonitrile. Alternatively the shale hydration inhibition agent may be the reaction product of a hydrogenation reaction of the product of the reaction of diethanolamine and acrylonitrile. The illustrative fluid is formulated such that the aqueous based continuous phase may be selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyarcylamides, and the like. A weighting material such as barite, calcite, hematite, iron

oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative fluid. The illustrative fluid may also include a wide variety of conventional components of fracturing fluids, such as propants such as sand, gravel, glass beads, ceramic materials and the like, acid release agents, fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

It should also be appreciated that the claimed subject matter inherently includes a composition that includes: an aqueous based continuous phase; a swellable shale material; and a shale hydration inhibition agent present in sufficient concentration to substantially reduce the swelling of the swellable shale material. Such a composition may be formed during the course of drilling a subterranean well, but also may be deliberately made if drill cuttings reinjection is to be carried out. In one illustrative embodiment, the shale hydration inhibition agent has the formula:



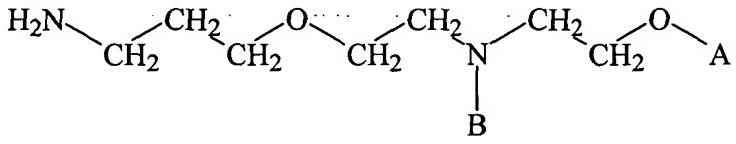
in which A is independently selected from H and $CH_2CH_2CH_2NH_2$; and in which B is independently selected from H, CH_2CH_2OH, $CH_2CH_2OCH_2CH_2CH_2NH_2$ and $CH_2CH_2CH_2NH_2$Alternatively, the shale hydration inhibition agent of the illustrative composition may be selected from



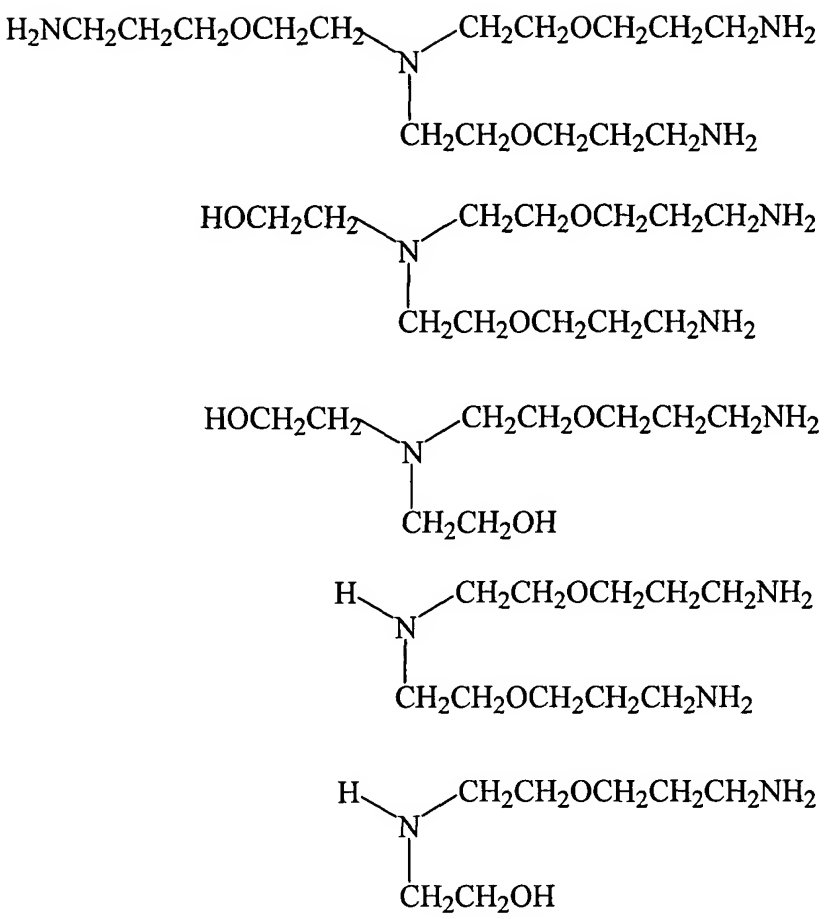
as well as mixtures of these. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of a hydrogenation reaction of the product of the reaction of triethanolamine and acrylonitrile. Alternatively the shale hydration inhibition agent may be the reaction product of a hydrogenation reaction of the product of the reaction of diethanolamine and acrylonitrile. The illustrative composition is formulated such that the aqueous based continuous phase may be selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyarcylamides, and the like. A weighting material such as barite, calcite, hematite, iron

oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative composition. The illustrative composition may also include a wide variety of conventional components of drilling and well bore fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

One of skill in the art should appreciate that the fluids of the claimed subject matter are useful during course of the drilling, cementing, fracturing, maintenance and production, workover, abandonment of a well or other operations associated with subterranean wells. In one illustrative embodiment, the fluids are utilized in a method involving the drilling a subterranean well through one or more subterranean formations containing a shale which swells in the presence of water. The illustrative method is carried out using conventional drilling means and techniques, however, the drilling fluid utilized is formulated to include: an aqueous based continuous phase; a weighting agent; and a shale hydration inhibition agent present in sufficient concentration to reduce the swelling of shale. In one illustrative embodiment, the shale hydration inhibition agent has the formula:



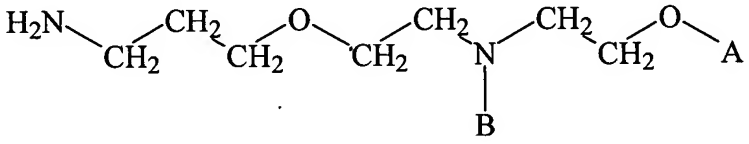
in which A is independently selected from H and $CH_2CH_2CH_2NH_2$; and in which B is independently selected from H, CH_2CH_2OH, $CH_2CH_2OCH_2CH_2CH_2NH_2$ and $CH_2CH_2CH_2NH_2$. Alternatively, the shale hydration inhibition agent of the illustrative composition may be selected from



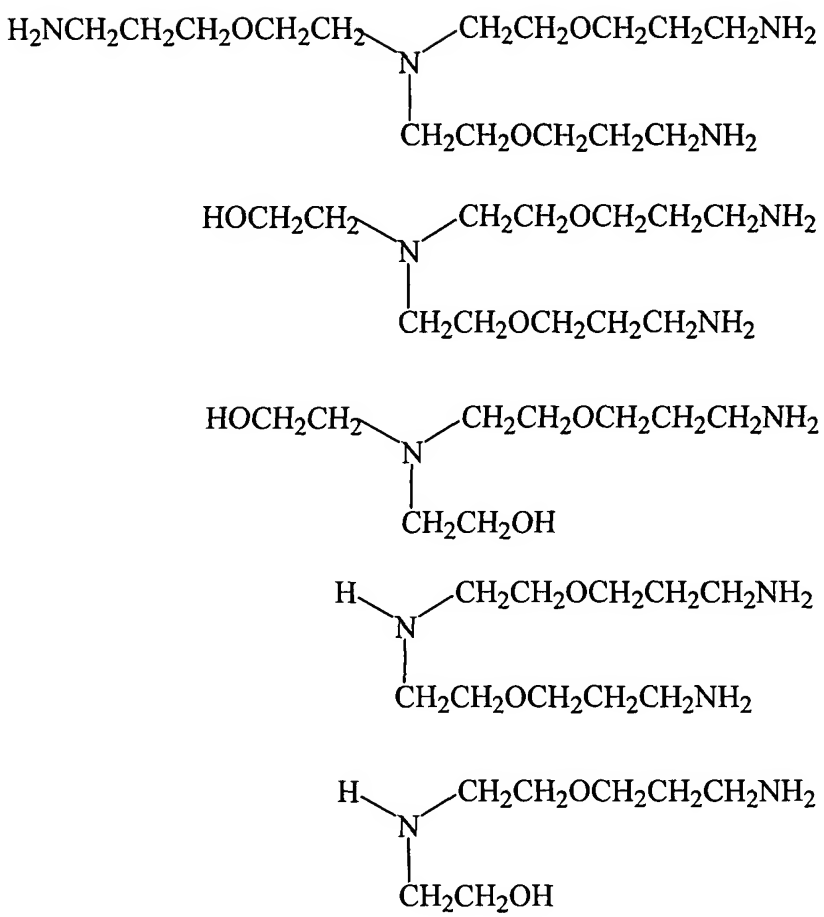
as well as mixtures of these. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of a hydrogenation reaction of the product of the reaction of triethanolamine and acrylonitrile. Alternatively the shale hydration inhibition agent may be the reaction product of a hydrogenation reaction of the product of the reaction of diethanolamine and acrylonitrile. The illustrative drilling fluid is formulated such that the aqueous based continuous phase may be selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyarcylamides, and the like. A weighting material such as barite, calcite, hematite, iron

oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative drilling fluid. The illustrative drilling fluid may also include a wide variety of conventional components of drilling and well bore fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

The claimed subject matter also includes a method of disposing of drill cuttings into a subterranean formation. As should be well known to one of skill in the art, this involves grinding the drill cuttings, which have been previously separated from the recirculating drilling fluid, in the presence of a fluid to form a slurry. The slurry is then injected by way of a well into a suitable subterranean formation for disposal. With this in mind a person of skill should appreciate that one illustrative embodiment of the claimed subject matter includes: grinding drill cuttings in a water-base fluid to form a slurry, in which the water based fluid is formulated to include: an aqueous based continuous phase and a shale hydration inhibition agent present in sufficient concentration to substantially reduce the swelling of the shale and then injecting the slurry into the subterranean formation designated for disposal of the cuttings. The shale hydration inhibition agent utilized in the formulation of the fluid is that which is substantive described above. That is to say the shale hydration inhibition agent utilized in one embodiment of the illustrative method has the formula:



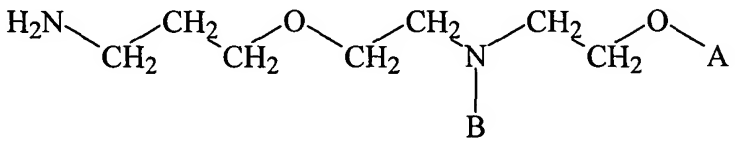
in which A is independently selected from H and $CH_2CH_2CH_2NH_2$; and in which B is independently selected from H, CH_2CH_2OH, $CH_2CH_2OCH_2CH_2CH_2NH_2$ and $CH_2CH_2CH_2NH_2$. Alternatively, the shale hydration inhibition agent of the illustrative method may be selected from



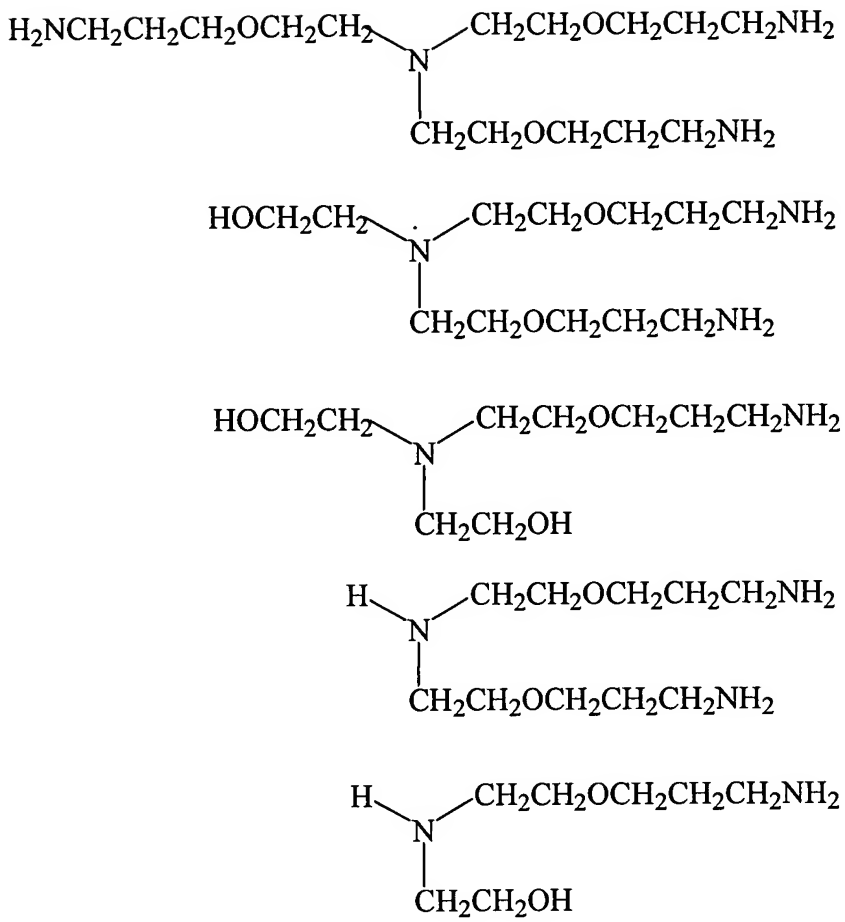
as well as mixtures of these. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of a hydrogenation reaction of the product of the reaction of triethanolamine and acrylonitrile. Alternatively the shale hydration inhibition agent may be the reaction product of a hydrogenation reaction of the product of the reaction of diethanolamine and acrylonitrile. The illustrative fluid is formulated such that the aqueous based continuous phase may be selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyarcylamides, and the like. A weighting material such as barite, calcite, hematite, iron

oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative fluid. The illustrative fluid may optionally include a wide variety of conventional components of drilling and well bore fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

It should also be appreciated by one of skill in the art that the claimed subject matter inherently includes a method of reducing the swelling of shale clay in a well comprising circulating in the well a water-base drilling fluid formulated as is substantially disclosed herein. One such illustrative fluid includes: an aqueous based continuous phase and a shale hydration inhibition agent present in sufficient concentration to reduce the swelling of the shale. That is to say the shale hydration inhibition agent utilized in one embodiment of the illustrative method has the formula:



in which A is independently selected from H and $CH_2CH_2CH_2NH_2$; and in which B is independently selected from H, CH_2CH_2OH, $CH_2CH_2OCH_2CH_2CH_2NH_2$ and $CH_2CH_2CH_2NH_2$. Alternatively, the shale hydration inhibition agent of the illustrative method may be selected from



as well as mixtures of these. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of a hydrogenation reaction of the product of the reaction of triethanolamine and acrylonitrile. Alternatively the shale hydration inhibition agent may be the reaction product of a hydrogenation reaction of the product of the reaction of diethanolamine and acrylonitrile. The illustrative fluid is formulated such that the aqueous based continuous phase may be selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyarcylamides, and the like. A weighting material such as barite, calcite, hematite, iron

oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative fluid. The illustrative fluid may optionally include a wide variety of conventional components of drilling and well bore fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

While the compositions and methods of this claimed subject matter have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the process described herein without departing from the concept and scope of the claimed subject matter. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the scope and concept of the claimed subject matter as it is set out in the following claims.